UNIVERSITI PUTRA MALAYSIA

KINETIC STUDY ON THE THERMAL DEGRADATION OF POLYVINYLPYRROLIDONE (PVP)

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By

ABDUEL HAMID N. EL GHEMI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfillment of the Requirement for the Degree of Master of Science

February 2003

DEDICATED

TO

My parents, my wife and my friends for their real help

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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February 2003

Chairman: Dr. Sa'ari Mustapha

Faculty: Engineering

Thermogravimetric analysis (TGA) data (thermogravimetric curves TG and derivative thermogravimetric curves DTG) were used to provide an alternative model of the kinetics of plastics waste degradation to the current model based on molecular weight distribution (MWD) measurement.

TGA models traditionally consist of assumed 'pseudo *first* order' kinetic equations. The thermal degradation kinetics of polyvinylpyrrolidone (PVP) was investigated by dynamic thermogravimetry, in a nitrogen atmosphere, over the temperature range 25-800 ^{o}C and at constant nominal heating rates of 5, 10, 20, and 30 ^{o}C/min, respectively. Two distinct mass change stages in the thermogravimetric analysis (TGA) curves indicated that the degradation of polyvinylpyrrolidone (PVP)

might be attributed to two reactions. The method developed to accommodate this kinetic study involved treating the data as a pseudo first-order reaction. The corresponding activation energies, frequency factors and reaction orders of the two reactions were determined. The TG thermgrams (TGA curves and DTG curves) obtained from TGA showed the same shape and trend at different heating rates of 5, 10, 20, and 30°C/min.

To accommodate this mechanism change, the data were treated as pseudo first-order reaction. A single first-order fit provided a good correlation of the data obtained at different heating rate for polyvinylpyrrolidone (PVP).

A simple relationship was developed to predict the activation energy for the pyrolysis process. The activation energy was found to be in good agreement with past experimental using polyvinylpyrrolidone (PVP).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEGAJIAN KINETIK PADA PENGURAIAN TERMAL POLIVINILPYRROLIDON (PVP)

Oleh

ABDUEL HAMID N. EL GHEMI

Februari 2003

Pengerusi: Dr. Sa'ari Mustapha

Fakulti: Kejuruteraan

Data analisis termogravimetrik (TGA) (iaitu lingkungan termogravimetrik TG dan lingkungan sisih termogravimetrik (DTG) adalah digunakan dalam projek ini untuk membekalkan satu model kinetic penguraiansisa plastic baru selain daripada pengukuran pertaburan jisim molekul yang didirikan baru-baru ini.

Model-model TGA secara tradisi mengandungi persamaan-persamaan dengan anggapan `pseudo tahap pertama'. Kinetik penguraian termal polivinylpyrrolidon (PVP) adalah dikaji dengan termogravimetrik dinamik, dalam atmosfera, melalui tempoh suhu 25-800 ^{o}C. dan kadar-kadar pemanasan norminal yang tetap 5,10,20 dan 30 ^{o}C/min masing-masaing. Dua tahap perubahan jisim yang berbeza dalam

lingkungan analisis termogravimetrik (TGA) menunjukkan penguraian polivinylpyrrolidon (PVP) mungkin disumbangkan oleh dua tindakbalas berlainan. Kaedah yang dibinakan untuk pengajian kinetic ini termasuk menganggapkan data tersebut sebagai satu tindakbalas `pseudo tahap satu'. Tenaga aktivasi, factor-faktor frekuensi dan tahap tindakbalas bagi kedua-dua tindakbals telah ditentukan. Termagrams TG (lingkungan-lingkungan TGA dan DTG) diperolehi daripada TGA menunjukkan bentuk dan trend yang serupa pada kadar-kadar pemanasan yang berlainan: 5,10, 20 dan 30 ^{o}C/min.

Untuk menepati perubahan mekanisme ini, data adalah diambil sebagai tindakbalas pseudo tahap pertama. Satu fit tunggal tahap pertama memberi korrelasi yang baik bagi data yang diperolehi di sebarang kadar pemanasan untuk polivinylpyrrolidon (PVP), tetapi perbezaan parameter-parameter dengan kadar pemanasan mesti diterima.

Bagi polivinylpyrrolidon (PVP), adalah diperhatikan data yang diperolehi telah memastikan hanya satu zon tindakbalas yang berlaku, di mana boleh dilihat dengan kawasan yang terdiri daripada dua garis lurus tahap pertama(kawasan I dan kawasan II) untuk setiap kadar pemanasan. Kawasan I telah dikenalpastikan
Sebagai tindakbals tahap pertama pada suhu yang rendah. Pada suhu yang tinggi, data-data juga boleh ditetapkan oleh satu tindakbals tahap pertama yang lain dan diwakili dalam kawasan II.

ACKNOWLEDGMENTS

Every praises is due to Allah alone, the Merciful and peace be upon his prophet who is forever a torch of guidance and knowledge for humanity as a whole.

I express my sincere gratitude to Dr. Sa'ari Mustapha for his scholarly guidance, valuable criticism and fruitful suggestions throughout this work. His critical review of the manuscript at several long sittings and assistance during thesis writing are gratefully acknowledged.

Also, I am indebted to Dr. Chuah Teong Guan and Dr. Ashraf Ali Omar for their generous help and guidance during the early stages of this investigation.

I certify that an Examination Committee met on 11th February 2003 to conduct the final examination of Abduel Hamid N. El Ghemi on his Master of Science thesis entitled "Kinetics Study on the Thermal Degradation of Polyvinylpyrrolidone (PVP)" in accordance with the Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as:

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Thesis Submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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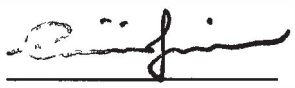

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Date: 8 MAY 2003

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations, which have been duly, acknowledge. I also declare that it has not been previously or concurrently submitted for any degree at UPM or other institutions.

ABDUEL HAMID N. EL GHEMI

Date: 1 April 2003

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LIST OF ABBREVIATIONS

PVP	Polyvinylpyrrolidone
TGA	Thermogravimetric Analysis
TG	Thermogravimetric
MSW	Municipal Solid Waste
PVC	Polyvinyl Chloride
NR	Natural Rubber
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis.
PCNSL	Phosphorylated Cashew Nut Shell Liquid
IPDT	Integral Procedural Decomposition Temperature
PAM	Poly allyl methacrylate
TVA	Thermal Volatilisation Analysis
PEA	Poly ethylene-co-acrylic acid
ENR	Epoxidized Natural Rubber
PP	Polypropylene
PE	Polyethylene
IR	Infrared
BR	Polybutadiene Rubber
MWD	Molecular Weight Distributions
PLA	Poly-L-lactide
DTG	Derivative Thermogravimetry
PIPA	Poly isopropenyl acetate
PdnPI	Poly (di-n-propyl-)
PdiPI	Poly (di-iso-propyl-)
PDnBI	Poly (di-n-butyl-)
PDiBI	Poly (di-iso-butyl-)
PDsBI	Poly (di-sec-butyl itaconate)
HDPE	High-Density Polyethylene
LDPE	Low-Density Polyethylene
LLDPE	Linear Low-density Polyethylene
PMMA	Poly (methyl methacrylate)
TA-FTIR	Thermal Analysis-Fourier Transform Infrared

CPE	Chlorinated poly(ethylene)
PVA	Poly vinyl acetate
$AlCl_3$	Aluminum chloride
PDMS	Polydimethylsiloxane
A	Preexponential Factor or Frequency Factor
R	Gas Constant (8.314 J/mol)
T	Temperature (^oC)
t	Time (s)
K	Reaction Rate
n	Order of Decomposition
Z	Frequency Factor
E	Activation Energy (J/mol)

CHAPTER I

INTRODUCTION

The last two and a half decades have seen a flurry of activities in the synthesis and development of high performance and high temperature polymers. The advanced materials are required for a diverse range of applications both industry and transportation including an aerospace, automotive and microelectronic industry. The application often requests the combination of properties including high glass transition temperatures, toughness, good adhesion, oxidative, thermal stability, and low dielectric constant. The polymer wastes are prime concern because the wastes are not easily degradable in nature as other wastes such as papers or organic wastes. Recycling of the polymer wastes is one of the attractive options to overcome the impact of the waste on the environment. However, high energy is requiring converting the wastes into usable part at high temperatures and shearing forces.

Most researches use black box approach for study on recycle plastics. Properties are measured after each processing step to determine the suitability of the material being processed for various applications. Little effort has been made to understand the actual happening to the polymer on a fundamental level. Conversely, not many scientists have examined the degradation of polymers by focusing specific time-temperature steps and monitoring some properties such as sample weight or molecular weight of polymers.

The type degradation of solid polymer is found analogous to the thermal cycles of resin during reprocessing. Small numbers of researchers have bridged the gap between these two areas to give a clear picture of the relationship between the degradation process and thermal cycles. Exposure to a certain temperature for a given what time could enable understanding of more precise engineering of materials for specific applications with less possibility of failure.

Most researches so far have focused on either structural aspect of the degradation or on property changes.

1.1 Properties and Application of Polyvinylpyrrolidone (PVP)

PVP exists as fine white or light yellow powder, odourless, tasteless and slightly hygroscopic. It can dissolve in water and a variety of organic solvents. It is generally used in cosmetics, surfactants, pharmaceutical industry, and binders for tablets, dispersants, thickeners and other related fields.

The chemical formula for PVP is $(C_6H_9NO)_N$ and the structural formula is as follows:

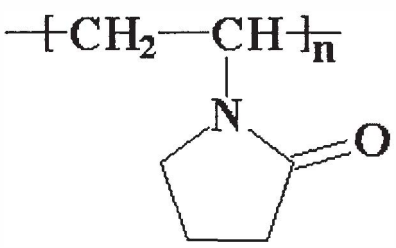

Table 1.1: The properties of Polyvinylpyrrolidone (PVP)

Molecular weight	44,000
Melting Point	130 °C
Specific Gravity	1.2
Residual Monomer	0.8%
Water	5%
Ash	0.02%
Viscosity of 5% aqueous solution at 25 °C	=2.4cp
PH	3-7 (100g/L, 20 °C)

PVP can be used as film-forming agent, viscosity-enhancement agent and adhesive. They are the key component of hair sprays, mousse, gels and lotions & solution. They are also convenience assistant in skin-care product, hair-dying reagent, shampoo, eye makeup, lipstick, deodorant, sunscreen and dentifrice.

Other Utilities includes: paint, coating, plastics, resin, clarifying agent, glass fiber, television tube and ink.

1.2 Pyrolysis Process

In cases where no other cause of a fire is apparent, pyrolysis of Polymer materials is an explanation that some investigators resort to. They reason that pyrolysis can occur in any area where Polymer materials are present, and requires only a source of heat, not necessarily a source of ignition. While it may seem to some like an easy out, the reality is that pyrolysis is a process that can and does lead to many fires.

A simple way of conceptualizing pyrolysis is to consider that hydrocarbons (methane, propane, gasoline, kerosene, etc.) are molecules consisting of hydrogen and carbon.

How does the pyrolysis of polymer matter lead to a fire? In essence, the breakdown of the Polymer matter means that you are creating a newer, more volatile fuel over a very long period of time. This fuel can auto-ignite, leading to a fire starting where there is no specific ignition source. The ignition of the pyrolyzed matter is often from the original heat source and as such, there is no change or unusual event that caused the fire to start.

1.3 Importance of Kinetic Study

Under appropriate conditions feed materials may be transformed into new and different materials, which constitute different chemical species. If this occurs only by rearrangement or redistribution of the constituent atoms to form new molecules, it means that a chemical reaction has occurred, where kinetic studies the mode and mechanism of reactions, the physical and energy changes involved and the rate of formation of products. It is the last mentioned area of interest, chemical

kinetics, which is of primary concern to us. Chemical kinetic searches for the factors that influence the reaction rate. It measures the rate and proposes explanations for the values found. The study is important for a number of reasons:

i. For physical chemists it is a tool for gaining insight into the nature of reacting systems for understanding how chemical bonds are made and broken, and for estimating their energies and stability.

ii. For the organic chemists the value of chemical kinetics is greater still because the mode of reaction of compounds provides clues to their structure. Thus relative strengths of chemical bonds and molecular structure of compounds can be investigated by this tool.

iii. It is the basis for important theories in combustion and dissolution and provides a method to study heat and mass transfer and suggests methods for tackling rate phenomena in other fields of study.

iv. For the chemical engineer the kinetics of a reaction must be known if to obtain satisfactorily design equipment.

Of course, if the reaction is rapid enough so that the system is essentially at equilibrium, the design is very much simplified. For this case kinetic information is not needed, and thermodynamic information alone is sufficient.

1.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a thermal analysis technique used to measure of the weight change of a material as a function of temperature and/ or time. TGA is commonly used to determine polymer degradation temperature, residual solvent levels, absorbed moisture content, and the amount of inorganic (non-combustible) filler in polymer or composite material composition.

1.4.1 Typical Application of (TGA)

- ***Physical Studies***.

  Reaction kinetics, information for the construction of phase diagrams, sorption measurements (and surface area determinations based upon gaseous adsorption techniques), volatility or sublimation measurements.

- ***Chemical Studies***.

  Desolation (particularly dehydration), purity determinations, the evaluation of catalysts and additives in materials, thermal and thermo-oxidative degradation, evaluation of precipitates, assessment of the effect of different atmospheres (i.e. corrosion and chemical resistance tests), identification of materials.

TG (Thermogravimetric) is used in all branches of pure and applied science, such as coal evaluation, food analysis and the development of plastics. Although it is impossible to consider all these applications, a few examples will illustrate the range

of the technique and the way in which TG results are interpreted. A precipitate suitable for gravimetric analysis has to be converted into a particular weighing form, i.e. it must have a known stoichiometric composition after drying or at a particular ignition temperature. The TG curve for such a precipitate indicates suitable drying or ignition temperatures by showing a constant-weight plateau.

1.5 Objectives of Study

The purpose of this research is to investigate the kinetic parameters of thermochemical conversion or the pyrolysis of the polyvinylpyrrolidone (PVP) using a thermogravimetric analysis (TGA) reaction (isothermal) over the temperature ranges of 30 to 800 ^{o}C on their thermal degradation behavior.

The specific objectives:

1. To study the kinetics of the PVP using thermal degradation.
2. To determine the kinetic parameters (activation energy, pre-exponential factor) using the thermogravimetric data.

1.6 Scope of Study

PVP is a material widely used as water-soluble polymer with excellent qualities. Because of its unique solubility, complexion ability and physiological inert, it has arrested great attention from scientific, industries and commerce since it was used as man-made plasma by the end of 1930s. PVP series products have also been widely used in various fields such as cosmetics, foodstuff manufacturing, drinks, adhesives, synthetic resins, textile dye printing, detergents, pigments, coatings, electronic materials, third time oil recovery in oilfield, and medical instruments (http://www.chinapvp.com/production.htm).

This study is carried out based on these both aspects the structural section will outline one group approach to polymer degradation including a novel technique dealing with molecular weight, and the property section will specifically focus on kinetics of polymer degradation.

The research seeks to better understand the thermal degradation of Polyvinylpyrrolidone (PVP) and explore also the kinetics of the process. One of the major studies of that project was the determination of the molecular weights and molecular weight distributions at each level of degradation.